CARBON CRYOGEL PRODUCTION FROM LIGNIN, IONIC LIQUID AND LIQUEFIED OIL PALM FROND AS CATALYST FOR ESTERIFICATION OF LEVULINIC ACID

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To my beloved family, friends and
all those who have contributed in this thesis.
This thesis is very special for me and all of you.
Alhamdulillah.

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ABSTRACT

Carbon cryogel synthesized from lignin, ionic liquid (IL) and mixtures of liquefied oil palm frond-ionic liquid (LOPF-IL), was used as an acid catalyst for esterification of levulinic acid in ethanol. Commercial lignin was reacted with furfural via sol-gel poly-condensation reaction at 90 °C for 30 min and the gel was freeze-dried and finally carbonized or calcined to produce carbon cryogel. Parametric study for the gel preparation was conducted to evaluate the carbon cryogel surface area and acidity. Similar parametric study was also performed on gel synthesis from IL and furfural. The selected gel condition of IL and furfural was applied for gel preparation from LOPF-IL and furfural. Nitrogen physisorption and temperature programmed desorption of ammonia measurements revealed the selected carbon cryogels obtained a large total surface area (>200 m^2/g) and high acidity (>10 mmol/g). The selected carbon cryogels from lignin-furfural (CCLF), IL-furfural (CCIL) and liquefied OPF-IL-furfural (CCOPF) were further characterized using thermogravimetric analyzer, Fourier transform infrared spectroscopy, x-ray diffraction and field emission scanning electron microscopy with energy dispersive x-ray spectrometry. The phase structure of the synthesized spherical carbon cryogel was amorphous, has micro structures (microspheres) and thermally stable. The synthesized CCLF, CCIL and CCOPF were tested as catalyst in the esterification of levulinic acid. Carbon cryogels showed high potential as an acid catalyst for levulinic acid esterification with above 70.0 mol.% yield of ethyl levulinate. The kinetic studies using CCLF and CCIL revealed the esterification of levulinic acid followed pseudo-first order kinetics and have low activation energy. Meanwhile, the thermodynamic parameters conferred the reaction was endergonic and more ordered.

ABSTRAK

Kriogel karbon dihasilkan daripada lignin, cecair ionik (IL), dan campuran cecair pelepah kelapa sawit-cecair ionik (LOPF-IL), telah digunakan sebagai pemangkin asid bagi pengesteran asid levulinik dalam etanol. Lignin komersial bertindak balas dengan furfural melalui tindak balas poli-kondensasi sol-gel pada 90 °C selama 30 min dan gel ini dibekukeringkan dan akhirnya dikarbonkan atau dikalsinkan untuk menghasilkan kriogel karbon. Kajian parameter terhadap penyediaan gel telah dilakukan bagi menilai luas permukaan dan keasidan karbon kriogel. Kajian parameter yang sama juga dilakukan terhadap sintesis gel daripada IL dan furfural. Keadaan gel IL dan furfural yang terpilih telah digunakan bagi penyediaan gel daripada LOPF-IL dan furfural. Pengukuran fisijerapan nitrogen dan penyahjerapan berprogram suhu ammonia mendedahkan kriogel karbon yang dipilih memperoleh jumlah luas permukaan yang tinggi (>200 m^2/g) dan keasidan (>10 mmol/g). Kriogel karbon yang dipilih daripada lignin-furfural (CCLF), IL-furfural (CCIL) dan cecair OPF-IL-furfural (CCOPF) selanjutnya dicirikan dengan menggunakan analisis termogravimetri, pembelauan sinar-x, spektroskopi inframerah transformasi Fourier, dan mikroskopi elektron pengimbas pancaran medan dengan spektrometri sinar-x sebaran tenaga. Struktur fasa kriogel karbon yang disintesis ialah amorfus, mempunyai struktur mikro (mikrosfera), dan stabil secara terma. CCLF, CCIL dan CCOPF yang disintesis telah diuji sebagai pemangkin dalam tindak balas pengesteran asid levulinik. Kriogel-kriogel karbon menunjukkan potensi tinggi sebagai pemangkin asid bagi pengesteran asid levulinik dengan hasil etil levulinat melebihi 70.0 mol.%. Kajian kinetik menggunakan CCLF dan CCIL mendedahkan pengesteran asid levulinik mengikut kinetik tertib pseudo-pertama dan mempunyai tenaga pengaktifan yang rendah. Sementara itu, parameter termodinamik menjelaskan bahawa tindak balas adalah endergonik dan lebih teratur.

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LIST OF ABBREVIATIONS

[AMIM][Cl]	–	1-allyl-3-methylimidazolium chloride
[BMIM][CH_3COO]	–	1-butyl-3-methylimidazolium acetate
[BMIM][Cl]	–	1-butyl-3-methylimidazolium chloride
[BMIM][HSO_4]	–	1-butyl-3-methylimidazolium hydrogensulfate
[BMIM][$MeSO_4$]	–	1-butyl-3-methylimidazolium methylsulfonate
[BMIM][N(CN)]	–	1-butyl-3-methylimidazolium methylsulfonate
[BMIM][OTf]	–	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[EMIM] [CH_3COO]	–	1-ethyl-3-methylimidazolium acetate
[EMIM][Cl]	–	1-ethyl-3-methylimidazolium chloride
$Ba(OH)_2$	–	Barium hydroxide
BET	–	Brunauer-Emmett-Teller
BHMF	–	bis(hydroxymethyl)furan
BJH	–	Barrett-Joyner-Halenda
CCIL	–	Carbon cryogel ionic liquid-furfural
CCLF	–	Carbon cryogel lignin-furfural
CCOPF	–	Carbon cryogel from liquefied OPF-IL
CO_2	–	Carbon dioxide
DMF	–	Dimethyleformamide
DMSO	–	Dimethyl sulfoxide
EDX	–	Energy dispersive X-ray
EFB	–	Empty fruit bunch

EL	–	Ethyl levulinate
FA	–	Furfuryl alcohol
FESEM	–	Field emission scanning electron microscopy
FTIR	–	Fourier Transform Infrared
GC-FID	–	Gas chromatography flame ionization detector
GPN	–	General-purpose novolak
GVL	–	γ-valerolactone
H_2O	–	Water
H_2SO_4	–	Sulfuric acid
HCl	–	Hydrochloric acid
HMF	–	5-hydroxymethylfurfural
HON	–	High *ortho* novolak
HPA-AC	–	Heteropoly acid activated carbon
HPLC	–	High performance liquid chromatography
HPN	–	High *para* novolak
IL	–	Ionic liquid
K_2CO_3	–	Potassium carbonate
KOH	–	Potassium hydroxide
KOH-AC	–	Potassium hydroxide activated carbon
LA	–	Levulinic acid
LOPF	–	Liquefied OPF
LOPF-IL	–	Liquefied OPF-ionic liquid
MARDI	–	Malaysian Agricultural Research and Development Institute
MPOB	–	Malaysian Palm Oil Board
NaOH	–	Sodium hydroxide
NH_3	–	Ammonia
OPF	–	Oil palm frond
OPT	–	Oil Palm Trunk
PEFB	–	Phenolated empty fruit bunch
PF	–	Phenol-formaldehyde

Rb_2CO_3	–	Rubidium carbonate
RF	–	resorcinol-formaldehyde
RHA	–	Rice husk ash
RI	–	Refractive index
SCB	–	Sugar cane bagasse
SEM	–	Scanning electron microscopy
TGA	–	Thermogravimetric analysis
TPA	–	Tungstophosphoric acid
TPD	–	Temperature programmed desorption
UV	–	Ultraviolet
XRD	–	X-ray diffraction

LIST OF SYMBOLS

°	–	Degree
%	–	Percentage
$\Delta G^{\ddagger}$	–	Gibbs energy of activation
$\Delta H^{\ddagger}$	–	Enthalpy of activation
$\Delta S^{\ddagger}$	–	Entropy of activation
°C	–	Degree Celsius
µL	–	Microliter
µm	–	Micrometer
‡	–	State of activated complex
A	–	Pre-exponential factor
C_A	–	Concentrations of levulinic acid
C_{AO}	–	Initial concentrations of levulinic acid
C_B	–	Concentrations of ethanol
C_C	–	Concentrations of ethyl levulinate
C_D	–	Concentrations of water
C_E	–	Final concentration of ethyl levulinate
C_L	–	Final concentration of levulinic acid
cm^3	–	Cubic centimeter
E_a	–	Activation energy
g	–	Gram
h	–	Hour
h	–	Planck’s constant
I_f	–	Weight of ionic liquid after recovery
I_i	–	Initial weight of ionic liquid
J	–	Joules

k	–	Reaction rate constant
K	–	Kelvin
$K^{\ddagger}$	–	Thermodynamic equilibrium constant
k_B	–	Boltzmann's constant
kJ	–	Kilojoules
kV	–	Kilovolt
L_f	–	Final weight of liquid product
M	–	Molar
m^2	–	Square meter
mA	–	Miliampere
M_E	–	Molecular weight of ethyl levulinate
mg	–	Milligram
min	–	Minutes
mL	–	Milliliter
M_L	–	Molecular weight of levulinic acid
Mmol	–	Milimolar
MPa	–	Megapascal
P	–	Total weight of ionic liquid and OPF
R	–	Gas constant
R^2	–	Regression coefficient
s	–	Seconds
t	–	Time
T	–	Temperature
v/v	–	Volume per volume
V_p	–	Final volume of product
W_i	–	Weight of levulinic acid
wt.	–	Weight
wt/wt	–	Weight per weight
X_A	–	Conversion of levulinic acid

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays, biomass energy becomes an attraction especially among the researches because it has high potentials as energy sources couple with the abundant availability. Biomass waste can be converted into renewable energy (bio-fuel and bio-power) or value added products (bio-product) (Sumathi *et al.*, 2008), as shown in Figure 1.1. There are many sources of biomass such as waste from plants and animals that can be used to produce energy for wide range of applications. Plants, animal and human are sources of biomass energy. This energy can be used in generating electricity, heating homes, fueling vehicles and provide process heat for industrial facilities (Demirbaş, 2001).

Biomass resources can be divided into three categories. The first is wastes (agricultural, crop residues, urban organic and urban wood wastes), the second is forest products (wood, logging residues, trees, and waste from forest cleaning) and the last category is the energy crops (consists of short rotation woody crops, grasses, starch crop, sugar crop, and oilseed crop) (Demirbaş, 2001). Besides, Yusoff (2006) have mentioned that the sources of biomass energy come from plant and animal

materials such as wood from the natural forest, waste from agricultural and forest industries, and domestic wastes. Furthermore, Effendi *et al.* (2008) has done a review on the biomass feedstock and they classified it into five categories which are woods (softwood, hardwood), forest residue (bark waste, peat moss, treetops, limbs), agriculture residues (bagasse, cashew nut shell, corn bran), industrial residues (paper and wood waste), and industrial lignins (organosolv lignin, lignosulphonate).

Thus, from the classification above, the biomass sources can be simplified into four major inputs as shown in Table 1.1. Lignocellulosic biomass that was come from the agricultural, forest and industrial sources was usually used in derived chemicals, fuels and materials. While for domestic biomass it can be used in fermentation in producing light hydrocarbon like methane. The by-product of fermentation such as bio-solid can be converted into a new material such as fertilizer.

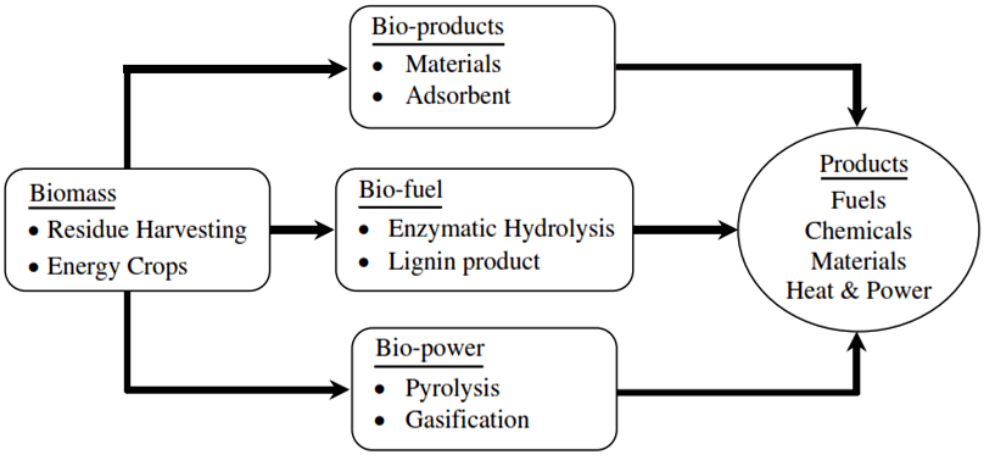

Figure 1.1 Biomass Initiatives as Renewable Energy (Sumathi *et al.*, 2008).

In Malaysia, large amount of palm oil residues are produced including oil palm fronds (OPF), empty fruit bunches (EFB) and also palm oil mill effluent (POME). Therefore, many researches in Malaysia are interesting in developed new products and chemical derivative from palm oil biomass since it is largely produced each year. Biomass from palm oil plantation are usually recycled or reused for other applications. Fronds, empty fruit bunches and palm oil mill effluent have already

been used in nutrient recycling (MPOB, 2012). A total of 10 tonnes pruned fronds are produced per hectare per year (MPOB, 2012). Thus, in this study, biomass OPF is utilized to produce carbon-based catalyst.

Table 1.1 : Examples of the biomass energy sources.

Sources	Example
Domestic	Human and food waste from urban and rural area
Livestock and agricultural	Plant crops residue, grasses, animal waste
Forest	Wood, logging residue, trees, bark and forest cleaning waste
Industrial	Industrial waste and lignin, paper and wood waste

Various types of homogeneous and heterogeneous catalysts including acid and base (organic and inorganic), metal oxide, and non-metal oxide (Alsalme *et al.*, 2008; Casas *et al.*, 2013; Gombotz *et al.*, 2012; Pasquale *et al.*, 2012; Yan *et al.*, 2013; Zhang *et al.*, 2012) are being synthesized. Recently, there is a prevalence of biomass-derived catalysts for application in green chemical processes (Chin *et al.*, 2012; Hidayat *et al.*, 2015; Man *et al.*, 2013; Olivier-Bourbigou *et al.*, 2010; Steinrück and Wasserscheid, 2015). In fact, carbon has been widely explored in the development of catalyst (Mar and Somsook, 2012; Shu *et al.*, 2009) instead of using as merely adsorbents only (Al-Omair and El-Sharkawy, 2007; Kadirvelu *et al.*, 2002; Malik, 2004). Carbon is suitable as catalyst support due to its high surface area and thermal stability (Baroutian *et al.*, 2010; Han *et al.*, 2010; Hara, 2010; Labrecque and Lavoie, 2011). These two properties are important to be applied as catalyst support in various types of reactions especially at high temperature.

Wide application of the carbon gel has attracted our attention in synthesis the carbon gel as the catalyst or catalyst supports. Carbon gel is one of the carbon types similar to activated carbon, carbon composite, and carbon film. However, the carbon gel is synthesized using chemicals and prepared by drying and carbonization process.

Different drying methods such as supercritical drying, freeze drying and evaporative drying would produce aerogels, cryogels, and xerogels, respectively. Carbon cryogel has good properties, characteristics and much potential due to its unique structure. There are some applications that used carbon cryogel which are column packing material in high performance liquid chromatography (HPLC) (Yamamoto *et al.*, 2002), anode material (Chao *et al.*, 2008) and support catalyst (Mukai *et al.*, 2005). This is due to the low cost in drying process compared to the supercritical drying. Besides, the freeze drying is capable in preserved the gel structure during the drying process by prevent the pore shrinkage.

The alternative method in order to substitute phenol was made by using lignin (Çetin and Özmen, 2002; Tejado *et al.*, 2007; Vázquez *et al.*, 1995) to produce organic gel with formaldehyde. Instead of using formaldehyde, aldehyde derivative such as furfural are possible to be applied for gel production in the presence of acid medium (Fink, 2005a). Both lignin and furfural are biomass-based side products of biofuel processes. The use of lignin and furfural in the synthesis of the carbon gel as catalyst is an alternative method for improving the sustainability in bio-fuel industry. Lignin-furfural mixture can be classified as furan resin that is synthesized via poly-condensation reaction in the presence of acid catalyst. The synthesized furan resin resulting in linear oligomers through the furan rings linkage by methylene and methylene-ether bridges (Fink, 2005b). Lignin itself has linked with monomers in their structures and the linkage with furfural produced more complex polymeric structures. In addition, the direct liquefied product of biomass which contains lignin that can be used as feedstock for gels synthesis.

As an approach for gel derivative from the biomass, the liquefaction process is conducted to dissolve high phenolic compound from biomass precursor. Previously, it was found that the liquefaction can be applied at a moderate temperature by using phenol as a solvent with an acid catalyst in order to produce phenolated lignin which is used in resin synthesis with formaldehyde (Ahmadzadeh *et al.*, 2009; Alma and Basturk, 2006; Lin *et al.*, 2004). Since phenol is a highly toxic chemical, other solvents have been applied in liquefaction, such as ionic liquids

(ILs). ILs show excellent solubility in terms of dissolving biomass. 1-butyl-3-methylimidazole hydrogen sulfate ([BMIM][HSO_4]) is one of the ILs that has been used for the extraction of lignin (Brandt *et al.*, 2011; da Costa Lopes *et al.*, 2013).

The different feedstocks are used in gel synthesis to produce a different type of gel structure. There is very limited study on resin or gel synthesis from ILs. Guo *et al.* (2015) has used the liquefied wood powder in ionic liquid mixture for resin synthesis by blending with phenol and formaldehyde. Thus, the finding was showed the IL has potential in resin synthesis. This progress becomes an alternative way to synthesized resin from mixture of IL biomass-derived compound. The resin is potentially applied for the carbon gel. The production of the carbon gel by using different feedstock and reaction condition used might influence the properties and structure of the carbon gel produce.

In the catalytic process, the synthesis of bio-fuel becomes attention to many researches in the world. Producing bio-fuel based chemical products from derivation of renewable sources such as biomass is an alternative technique to replace petroleum resources due to the depletion of fossil fuel. Levulinic acid is one of the organic acids that show high potential to be derived from lignocellulosic biomass. Levulinic acid is suitable for fuel additive derivation such as ethyl levulinate via esterification with ethanol. The synthesized ethyl levulinate might be used as an oxygenate additive in fuels (Pasquale *et al.*, 2012) and diesel miscible biofuel (up to 5 wt.%) (Nandiwale *et al.*, 2013). It is functioning as fuel additive in order to improve the engine performance, fuel handling and stability, and fuel quality which is help to reduce the production of carbon monoxide. Besides, the ethyl levulinate also can be used as flavoring agent and precursor for production of γ-valerolactone (GVL) (Maldonado *et al.*, 2012b).

The catalytic process requires good performance of catalyst which has good chemical properties and stability. The application of the carbon cryogel as heterogeneous catalyst in the esterification reaction becomes an alternative method in

substituted the usage of homogeneous acid catalyst. The derivative of carbon cryogel from biomass is an approach in tailoring good properties of the carbon-based catalyst. As comparison with carbon-based catalyst from direct carbonization of biomass and their modification, the carbon cryogel derived from biomass shows more advantages in their properties and stability. This is due to the chemical linkage in the carbon cryogel structure during the gel synthesis. The drying and thermal heating process in carbon cryogel preparation is helpful in improved the surface properties.

1.2 Problem Statement

Every year, lignocellulosic biomass generates high production of waste. Nowadays, the biomass is applied for fuel and chemical production due to high potential of producing bio-fuel, bio-gas and chemicals. However, in biomass and biofuel industry, the reaction process still produces byproduct which becomes an unused chemical for industries due to less functioning application. Therefore, in order to reduce waste and byproduct from industries, the use of these abundant are required in order to generate beneficial material as well as retain sustainability. Organic catalyst, especially derivative from lignocellulosic biomass, is currently being developed for application in reaction engineering. The organic catalyst is referred to carbon-based catalyst which is potentially derived from biomass such as activated carbon and carbon gel.

In carbon gel synthesis, phenol has been commonly used with formaldehyde to produce gels (Mukai *et al.*, 2005; Poljanšek and Krajnc, 2005; Scherdel and Reichenauer, 2009). However, the use of chemical compound such as phenol and formaldehyde are hazardous and give bad impact to human health. Instead of using phenol and formaldehyde, gels could be synthesized by using phenol and formaldehyde derivatives. The synthesis of organic gels via phenol and aldehyde

derivatives compounds might give different properties and reactivity to the organic gel compound. Lignin as the byproduct from the biomass conversion is potentially derives the organic gel for preparation of carbon gel. Previously, lignin (Çetin and Özmen, 2002; Tejado *et al.*, 2007; Vázquez *et al.*, 1995), tannin (Grishechko *et al.*, 2013b; Szczurek *et al.*, 2011), and resorcinol (Babić *et al.*, 2004; Czakkel *et al.*, 2005; Tamon *et al.*, 1997) have been used to produce organic gels as another alternative to substitute and reduce phenol usage. On the other hand, formaldehyde derivatives such as paraformaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, glyoxal, trioxane, furfural, and furfurol have been tested to produce phenolic resins (Fink, 2005a). For instance, substitution of phenol and formaldehyde derivatives with tannin and furfural (Kraiwattanawong *et al.*, 2007) and phenolic polymer and furfural (Pekala *et al.*, 1995) have produced organic gels.

In Malaysia, Oil palm frond (OPF) is one of the largest productions of palm oil wastes in palm oil plantation after empty fruit bunch. Many efforts have been done in order to reduce the capacity of OPF. For example, preparation of activated carbon from OPF for bentazon adsorption from aqueous solutions (Salman and Hameed, 2010), glucose recovery using OPF via pretreatment by hot compressed water (Goh *et al.*, 2010) and pulp production from OPF (Wanrosli *et al.*, 2007). This effort might help to reduce the remaining waste materials by converting the waste into beneficial products. The biomass conversion through the liquefaction process for carbon cryogel production is one of the alternatives to produce useful material. The liquefied product with high content of lignin are consists of phenol derivative which could be used to substitute phenol into gel synthesis.

Over the last decade, the derivative product from biomass through the liquefaction was explored in the synthesis of resin. However, the synthesis process involves phenol as a solvent for the liquefaction process. Liquefaction process is usually occurred at high temperature in order to produce bio-oil (Akhtar *et al.*, 2010; Tymchyshyn and Xu, 2010). The bio-oil which is rich with phenolic compound is also used in resin synthesis. It was reported that there has an alternative in processing the biomass through liquefaction in phenol at moderate temperatures in

the presence of an acid catalyst to produce phenolated lignin (Ahmadzadeh *et al.*, 2009; Alma and Basturk, 2006; Lin *et al.*, 2004). The phenolated lignin also has been used in gel synthesis with formaldehyde.

Another alternative is used in this study by applied ionic liquid as a solvent for the liquefaction. The ionic liquid shows high potential in liquefy the biomass due to the excellent solubility for dissolving biomass. Although the ionic liquid is good in dissolving the biomass, nevertheless, the potential of using ionic liquid in gel synthesis is still unclear. Though, there is a study that has using the functional ionic liquid with liquefied wood powder mixture for resin production (Guo *et al.*, 2015), however, phenol and formaldehyde still involve in liquefied mixture for resin synthesis. Therefore, the detail study of gel synthesis from ionic liquid should be conducted as an alternative to replace phenol in resin synthesis. It is predicted that, a successful work of gel synthesis from the ionic liquid might open a different pathway in gel derivative by using ionic liquid with biomass mixture. Therefore, the gel can be used in preparation carbon gel. The chemical properties of ionic liquid as a solvent and also pseudo homogeneous catalyst can influence the properties of carbon cryogel production. The gel synthesis and carbon production from the ionic salt is a good alternative in liquid sample conversion into solid structure which it can be used in another application. The synthesis of the carbon cryogel from the ionic liquid and their mixture with the biomass-derivative product is studied toward the application as acid catalyst.

High production of biodiesel requires an additive in order to improve their quality and performance. The esterification reaction of levulinic acid is carried out in the presence of acid catalyst to produce ethyl levulinate which can be used as additive. However, the use of homogeneous acid catalyst shows some drawbacks although high yield of product is achieved. Therefore, the application of heterogeneous catalyst is required to improve the synthesis of ethyl levulinate. Fernandes *et al.* (2012) has mentioned that the heterogeneous catalyst is required for easy catalyst separation and can be reused several times, instead of using mineral acid that is corrosive to the equipment and need further neutralization process.

Therefore, appropriate heterogeneous catalyst is required during the reaction in order to overcome the problem in ethyl levulinate synthesis. High stability, surface area and acidity of the carbon cryogel catalyst are useful to solve this problem.

Many catalysts have been developed and carbon-based catalyst shows the potential to be applied as the heterogeneous organic catalyst. High acidity and surface area presented by carbon cryogel shows the advantage to be used as a solid acid catalyst for the esterification reaction in synthesizing a fuel additive. Besides, the carbon cryogel is possibly derived from a low cost biomass feedstock give benefit towards the production. Therefore, the carbon cryogel was used as an alternative catalyst instead of using non-organic catalyst in the esterification reaction.

1.3 Research Hypotheses

The carbon cryogel is potentially derives by using phenolic compound such as the lignin. The reactivity of the lignin could be increased by conduct the reaction with furfural in the presence of concentrated acid medium. The lignin and furfural is possibly linked through the electrophilic substitution of lignin phenylpropanoid with the carbonyl group of furfural as explained by Dongre *et al.* (2015). This linkage mechanism is related to the idea of gel production from [BMIM][HSO_4] ionic liquid. The electrophilic substitution of the imidazole structure of the ionic liquid with the carbonyl group of the furfural is possibly occurs to obtain the linkage between both chemical. The study of gel synthesis from ionic liquid is conducted as an initial step for the preparation of the biomass-derived carbon cryogel. This is because the ionic liquid will be applied with liquefied oil palm frond as a mixture for production of the carbon cryogel.

Carbon cryogel production is depends on the gel synthesis and preparation method. In previous study, the application of solvent exchange with t-butanol was used to prevent the pore shrinkage of the gel structure. However, the usage of *t*-butanol can be avoiding as the production of monolith carbon is not required. The synthesis and drying process should be controlled to produce carbon cryogel of different shapes and sizes for various applications. There are some factors might influence the surface area of carbon cryogel which are feedstock ratio, amount of water and acid loading. Besides, the heating condition in preparation of carbon cryogel also can affect their surface area.

All the gel production is from lignin, ionic liquid and the liquefied OPF-ionic liquid (LOPF-IL). There are connected via cross-linking network. In their structure, the chemicals were linkage through neither dimethyl-ether nor methylene bridges. The dried gel (cryogel) will be formed after freeze drying process and obtained the carbon after the heating process at high temperature. The carbon cryogel will produce large surface area and high acidity with good thermal stability. Thus, the carbon cryogel produce can be utilized as acid catalyst in the esterification reaction of levulinic acid in ethanol.

As for the esterification reaction, all the carbon cryogel consists of Brønsted acid site which is potentially applied as acid catalysts. High surface area and acidity can enhance the levulinic acid esterification in ethanol to produce high yield of ethyl levulinate. The kinetic and thermodynamic study is performed on the levulinic acid conversion to reduce the activation energy in the presence of carbon cryogel and study their reaction behavior.

1.4 Research Objectives

Based on the carbon cryogel production, the synthesis process involves the production of three different types of carbon cryogel catalyst for the study on ethyl levulinate production. The objectives of the research are:

i. To synthesize and characterize of the carbon cryogel production from commercial lignin, 1-butyl-3-methylimidazole hydrogen sulfate ionic liquid [BMIM][HSO_4], and liquefied oil palm frond-ionic liquid mixture (LOPF-IL).

ii. To study the effect of parameters on esterification reaction of levulinic acid.

iii. To perform kinetic and thermodynamic studies of reaction in the presence of carbon cryogel as catalyst.

1.5 Scope of Research

In order to achieve the research objectives, the scopes of research were drawn as follow:

i. Carbon cryogel was synthesized from commercial lignin and furfural via sol-gel poly-condensation reaction at 90 °C for 30 min followed by drying and thermal treatment. For gel synthesis, the process conditions were

initially investigated at various lignin to furfural ratio (0.77 to 1.43), lignin to water ratio (0.5 to 1.5), and acid concentration (2M to 8M). As the preparation for carbon cryogel, the temperature and time for carbonization (300 to 700 °C; 1 to 5 h), and calcination (300 to 550 °C; 1 to 5 h) processes were studied to determine the optimum condition. The effect of parameters study was observed toward the total surface area and acidity. The carbon cryogel that was produced from lignin and furfural was labelled as CCLF.

ii. Carbon cryogel also was synthesized from [BMIM][HSO_4] ionic liquid (IL) through the thermal reaction at 100 °C, 1 h followed by drying and thermal treatment. The parameters studies of furfural to ionic liquid ratio (0.75 to 1.50), water to ionic liquid ratio (0.063 to 0.25), acid amount (0.5 to 2.0 mL) and calcination temperature (350 to 500 °C) and time (1 to 2.5 h) were observed on the surface area and acidity of carbon cryogel. The carbon cryogel that was produced from ionic liquid and furfural was labelled as CCIL. The reaction between ionic liquid with furfural was studied on carbon cryogel production as an initial step to produce the carbon cryogel from liquefied oil palm frond (OPF) in ionic liquid mixture.

iii. As for the liquefaction, the parameters of temperature (110 to 180 °C), time (0.5 to 2.0 h) and IL to OPF ratio (2 to 4) were investigated towards the liquefied OPF yield. After the liquefaction, the mixture of liquefied OPF and ionic liquid were produced and directly utilized in gel synthesis. Therefore, investigation on carbon cryogel from ionic liquid as stated before is important to avoid the problem on carbon cryogel synthesis from liquefied OPF-IL mixture. The same reaction condition of CCIL synthesis was applied to produce carbon cryogel from liquefied OPF-IL mixture. The carbon cryogel produce from liquefied OPF-IL (LOPF-IL) mixture with furfural is known as CCOPF.

iv. The CCLF, CCIL and CCOPF were characterized using N_2 adsorption and desorption (BET), temperature programmed desorption of ammonia (NH_3-TPD), thermogravimetric analyzer (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and field emission scanning electron microscope with energy dispersive X-ray Spectrometry (FESEM-EDX). Through the characterization studies, the physical and chemical properties of carbon cryogel can be explained. Besides, the surface structure of the carbon cryogel also was observed.

v. The carbon cryogel was applied as acid catalyst in derived ethyl levulinate from the levulinic acid. The catalytic testing and parameters studies are conducted in the presence of synthesized carbon cryogel. Four reaction parameters were studied which are carbon cryogel loading (CCLF and CCIL – 5 to 35 wt.%, CCOPF – 15 to 35 wt.%), ethanol to levulinic acid molar ratio (5 to 30), reaction temperature (CCLF – 78 to 170 °C, CCIL – 78 to 200 °C) and reaction time (CCLF – 1 to 8 h, CCIL and CCOPF – 1 to 6 h). The condition was selected based on the response of ethyl levulinate yield and levulinic acid conversion. All the parameters were studied by CCLF and CCIL in batch reactor system. However, the CCOPF only performed in the reaction with reflux experiment setup at fixed reaction temperature as preliminary study.

vi. The kinetic and thermodynamic studies were conducted on the reaction in the presence of CCLF and CCIL. The kinetic study was performed using the pseudo homogenous approach in order to determine the reaction rate constant and activation energy. The pseudo-zero, pseudo-first and pseudo-second order kinetic models were performed and compared. The models were validated using the linear plot of the kinetic models and the parity plot of the predicted data and actual data. As for the thermodynamic study, the parameters such as the enthalpy of activation, entropy of the activation and the Gibbs energy of activation were determined.

1.6 Research Significance

This research is utilized carbon cryogel (CCLF, CCIL and CCOPF) as benign catalyst for the ethyl levulinate production from the levulinic acid and ethanol. The production of carbon cryogel as new carbon-based catalyst is applied for the replacement of the homogeneous acid catalyst such as H_2SO_4 in the esterification reaction. High acidity and surface area of carbon cryogel catalyst was produced to enhance the reaction toward the high production of ethyl levulinate. Due to high thermal stability of the carbon cryogel makes their application more useful as catalyst. The optimum parameters on the gel synthesis and carbon preparation can be used in produce the carbon cryogel more efficiently and particularly useful for baseline study by using other feedstocks and for upscaling process. The selected condition of ethyl levulinate synthesis in the presence of carbon cryogel can give information in conducting the reaction with better utilization of resources especially for large scale processes. In addition, the kinetic and thermodynamic parameters obtained from this study can be used to describe the levulinic acid conversion under the influence of different reaction temperatures. Based on the overall results, the carbon cryogel is highly potentially as super acid carbon-based catalyst in derived the ethyl levulinate.

1.7 Research Outline

This thesis is divided into 7 chapters and begins with an introduction as presented in Chapter 1. The introduction is consists the research background, the related problems in the research area, the hypotheses, research objectives and scope, and the significance of this research. As in the Chapter 2, the literatures is describe the previous research works related to the biomass conversion, ionic liquid production, resin and carbon gel studies, and levulinic acid esterification. Next, Chapter 3 elaborates the details on experimental procedures such as the carbon gel

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